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INFLUENCE OF DEFLOCCULANT ON THE ISOELECTRIC POINT
OF REFRactory POWDERS
- CONSIDERATIONS ON THE ACTION OF DEFLOCCULANT
FROM THE VIEWPOINT OF SOLID-LIQUID INTERFACIAL PROPERTIES -

Yoichi Naruse, Kimio Sembra, Sukekazu Kiwaki and Masaaki Mishima



Translation of "Funtai no todeten ni oyobosu bunsanzai no eikyo
- Kaimen tokusei kara mita bunsanzai no sayo ni kan-suru kosatsu -"
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| 16. Abstract Isoelectric point changes in suspensions of refractory materials vis-a-vis the role of deflocculants used in monolithic refractories were investigated by considering the mineral compositions and adsorbed ions in four kinds of clay. Three types of curves represented the relation between the isoelectric point and the deflocculant. The surface charge of clay particles in the suspensions became negative as a result of the deflocculant, since the isoelectric point of suspensions decreased as the deflocculant was added. The isoelectric point changes of calcined alumina were also compared with those of the clays, and a similar phenomenon was observed, except that the deflocculant dispersed the calcined alumina better than it did the clays. A simple model was used to analyze the results. | | | |
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1. Introduction

Various types of additives are generally used in monolithic ref- /3* ractories to give them workability. Among them, the so-called defloc- culants improve their workability by operating on the fine-powder com- ponents in their mix. However, the action of deflocculants is ext- remely sensitive to their contents. If their contents are excessive, this will likely result in improvement of the workability with deteri- oration of the general physical properties, or in some cases the work- ability, on the contrary, may deteriorate. Consequently, in using these additives it will be important to learn their optimal contents, which may be determined in terms of a balance between both the work- ability and the physical properties.

In this report, we give the results of tests concerning the dis- persing action and also the optimal contents of deflocculants. The tests were carried out by investigating the influence of deflocculants on the isoelectric point of refractory powders.

2. Tests

In a system consisting of refractory powders (chiefly oxides) and water, when the total charges of each of the ions (H^+ and OH^-) occupying positive and negative adsorption sites on the surfaces of the suspended particles are balanced, the virtual surface charge of the whole will be zero. The pH at this time is called the isoelectric point. If for some reason the particle surfaces are charged in the

*Numbers in the margin indicate pagination in the foreign text.

quantitative findings, we envisioned a simple model and attempted an analysis of the changes in the surface potential caused by the addition of the deflocculant.

3. Discussion

3.1. Model

Adsorption of the deflocculant particles (ions) is considered as the cause of the changes of the surface potential ϕ of the suspended particles. Here let us divide ϕ , as shown below, into a part ϕ_o which is unrelated to the deflocculant and a part ϕ_D which is caused by adsorption of the deflocculant:

$$\begin{aligned}\phi &= \phi_o + \phi_D \\ \phi_D &= \phi_D(m) \quad \text{if } m > 0 \\ &= 0, \quad \text{if } m \leq 0\end{aligned}$$

m : Number of deflocculant particles

As for the changes in the surface potential caused by addition of the deflocculant, we consider an increase of potential caused by adsorption of the deflocculant to the adsorption sites on the particle surfaces as well as a decrease of potential caused by desorption of the deflocculant which has already been adsorbed. We assume the following equation:

$$\frac{d\phi}{dm} = qNm - q(N_o - N) \quad \dots \dots \dots (1)$$

If we further assume that all of the deflocculant added is adsorbed and none of it remains in the liquid:

$$N_o = N + m \quad \dots \dots \dots (2)$$

The following equation is derived from equations (1) and (2):

$$\frac{d\phi}{dm} = q(N_o - m)m - qm \quad \dots \dots \dots (3)$$

Here,

q : Coupling constant of clay and deflocculant

\bar{q} : Dissociation constant of clay and deflocculant

N_o : Total number of adsorption sites on clay surface

N : Number of empty sites on clay surface

Table 1 Properties of clays studied.

| Clay Kind | A - 1 | A - 2 | B - 1 | B - 2 |
|---------------------------------------|-------|-------|-------|-------|
| Sieve Analysis (wt. %) | | | | |
| >44 μ m | 12.9 | 4.1 | 5.1 | 3.6 |
| 44~25 | 7.1 | 10.1 | 8.1 | 2.0 |
| 25~10 | 6.3 | 17.1 | 18.9 | 3.3 |
| 10~5 | 28.9 | 13.6 | 13.1 | 4.4 |
| 5~0 | 44.8 | 55.1 | 54.8 | 86.7 |
| Exchangeable Cation (m.e./100g) | | | | |
| Mg ⁺⁺ | 1.9 | 5.6 | 2.6 | 6.0 |
| Ca ⁺⁺ | 2.7 | 4.6 | 4.1 | 11.3 |
| Na ⁺ | 0.4 | 0.5 | 0.3 | 0.2 |
| Ka ⁺ | 0.6 | 0.6 | 0.3 | 0.5 |
| total | 5.6 | 11.3 | 7.3 | 18.0 |
| SO ₄ ⁻⁻ (wt. %) | 0.004 | 0.051 | 0.002 | 0.021 |
| Mineral Composition | | | | |
| Kaolin | ○ | ○ | ○ | ○ |
| Quartz | ○ | ○ | ○ | ○ |
| Feldspar | ○ | × | × | × |
| Mica | ○ | ○ | ○ | ○ |
| Montmorillonite | × | × | ○ | ○ |
| Inters. Mica-Mont. | × | × | ○ | ○ |

Table 2 Property of sodium pyrophosphate (SPP) used as deflocculant.

| Purity | Cl ⁻ | SO ₄ ⁻⁻ | Solubility | pH |
|-------------|-----------------|-------------------------------|--------------|---------------|
| >97.0 wt. % | <0.5 wt. % | <0.08 wt. % | 6.2 g (20°C) | ~10(1%-soln.) |

2.2. Measuring Methods

The deflocculant was added to the refractory powder suspensions (clay concentration 2 g/100 cc) with a concentration of m% by weight with respect to the clay and was left to stand for a definite time. The deflocculant added was adsorbed onto the surfaces of the suspended particles during this time, and the isoelectric point was then measured by the method of Mular and Roberts [2]. The pH meters used were 801A digital pH/ion meters (manufactured by Orion Research Inc.). Measurements were made with the suspension temperature in a range of 25±1°C so that temperature changes would have a negligible influence on the measurement results.

2.3. Measurement Results

The relationship between the isoelectric point and the deflocculant content (the I-m curve) may generally be divided into the three types illustrated in Fig. 1.

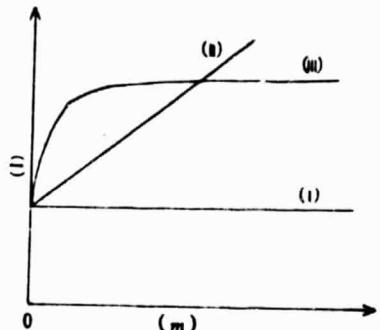


Fig. 1 Possible behaviors of I-m curves.

Curve (i)

The deflocculant plays no role in the formation of the surface potential of the suspended particles. That is, either none of it is adsorbed onto the particle surfaces, or its adsorptive power is extremely weak in comparison with H^+ , OH^- , etc.

Curve (ii)

The deflocculant added is proportionally adsorbed onto the particles and causes their surface potential to change in a linear fashion.

Curve (iii)

During the initial period of addition (the region where small amounts are added), the deflocculant is relatively well adsorbed and changes the surface potential. However, after a certain content has been exceeded, the potential gradually approaches a constant potential.

Curves (ii) and (iii) here apply to deflocculants which operate so as to move the surface potential of the particles in the positive direction. If the deflocculant is one which operates so as to move the surface potential in the negative direction, one need only assume a curve descending towards the right.

The isoelectric point values obtained for four clays are shown in Table 3.

Table 3 Isoelectric point obtained for the clays with various contents of deflocculant.

| SPP content | A - 1 | A - 2 | B - 1 | B - 2 |
|-------------|-------|-------|-------|-------|
| 0 wt. % | 5.85 | 4.90 | 5.30 | 6.95 |
| 0.25 | 5.50 | 5.15 | 5.00 | 7.15 |
| 0.50 | 5.55 | 4.65 | 5.15 | 6.65 |
| 1.00 | 5.00 | 4.60 | 4.75 | 6.00 |
| 2.00 | 4.75 | 4.15 | 4.85 | 5.40 |
| 4.00 | 4.40 | 4.00 | 4.80 | 4.85 |

Their variations are illustrated in Figs. 2 and 3.

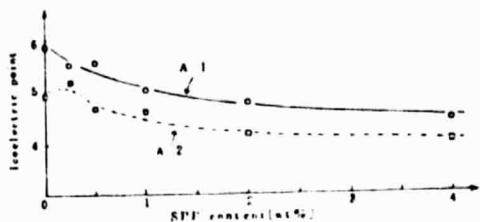


Fig. 2 Isoelectric point of sample A-1 and A-2 as a function of SPP content. Montmorillonite is not in these clays.

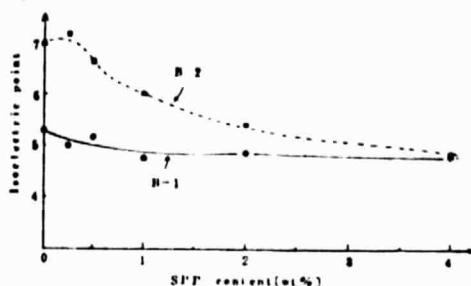


Fig. 3 Isoelectric point of sample B-1 and B-2 as a function of SPP content. Montmorillonite is included in these clays.

The following results are obtained if we compare the variations of the isoelectric point following the addition of the deflocculant SPP with the characteristics of the clays studied as shown in Table 1:

(i) In the region where small amounts (about 0.5% by weight or less) are added, the amount of adsorbed ions has a stronger influence than the presence or absence of montmorillonite.

(ii) In clays A-1 and B-1, which have small amounts of adsorbed ions, the isoelectric point decreases monotonically as the deflocculant is added.

(iii) In clays A-2 and B-2, which have large amounts of adsorbed ions, the isoelectric point does not change in the region where small amounts are added. On the contrary, there is rather a tendency for it to increase.

(iv) Regardless of the differences in their mineral composition /5 and the amounts of their adsorbed ions, the isoelectric points of the four clays decrease, and their behavior is similar to that of curve (iii) in Fig. 1.

Because the isoelectric points decreased as a result of addition of the deflocculant SPP, it is believed that the surface potential of the clay particles increased in the negative direction. However, only conclusions on the order of those in (i) - (iv) above can be reached on the basis of Figs. 2 and 3. Therefore, in order to obtain more

quantitative findings, we envisioned a simple model and attempted an analysis of the changes in the surface potential caused by the addition of the deflocculant.

3. Discussion

3.1. Model

Adsorption of the deflocculant particles (ions) is considered as the cause of the changes of the surface potential ϕ of the suspended particles. Here let us divide ϕ , as shown below, into a part ϕ_0 which is unrelated to the deflocculant and a part ϕ_D which is caused by adsorption of the deflocculant:

$$\phi = \phi_e + \phi_D$$

$$\phi_D = \phi_D(m) \text{ かつ } \phi_D(0) = 0.$$

m: Number of deflocculant particles

As for the changes in the surface potential caused by addition of the deflocculant, we consider an increase of potential caused by adsorption of the deflocculant to the adsorption sites on the particle surfaces as well as a decrease of potential caused by desorption of the deflocculant which has already been adsorbed. We assume the following equation:

If we further assume that all of the deflocculant added is adsorbed and none of it remains in the liquid:

The following equation is derived from equations (1) and (2):

$$\frac{d\phi}{dm} = q(N_0 - m)m - \bar{q}m \quad \dots \dots \dots \quad (3)$$

Here.

g: Coupling constant of clay and deflocculant

q : Dissociation constant of clay and deflocculant

N : Total number of adsorption sites on clay surface

N: Number of empty sites on clay surface

(a) If q and \bar{q} are constant without regard to m , it will be possible to integrate equation (8) immediately:

$$\int_{\phi_0}^{\phi} d\phi = \int_0^m dm [q(N_e - m)m - \bar{q}m] = -\frac{q}{3}m^3$$

$$+ \frac{(qN_e - \bar{q})}{2}m^2$$

$$\therefore \phi - \phi_0 = -\frac{q}{3}m^3 + \frac{(qN_e - \bar{q})}{2}m^2 \quad \dots \dots \dots (4)$$

(b) If q and \bar{q} depend on m , the following form is assumed:

$$q = q_0 e^{-km}, \quad \bar{q} = q_0 (1 - e^{-km})$$

If we substitute this in equation (8) and integrate it in the same way as in (a), we obtain:

$$\phi - \phi_0 = Q e^{-km}$$

Here Q is a polynomial of m . If, for the sake of simplicity, we ignore the secondary or higher terms:

$$\phi - \phi_0 = A m e^{-km} \quad \dots \dots \dots (5)$$

Here, A is the q_0 function of constant A .

If we assume that there is a linear relationship between the iso-electric point and the potential, corresponds to $\phi - \phi_0$ in (4) and (5). ΔI is the difference between the isoelectric point when the deflocculant is not added and that when it is added in an amount of m by weight. Consequently, in (a) we will obtain a straight line if we plot $\Delta I/m^2$ against m , and in (b) we will obtain a straight line if we plot $\log(\Delta I/m)$ against m .

Table 4 Calculated values of Δl , $\Delta l/m$ and $\Delta l/m^2$ for sample A-1.

| m | I | Δl | $\Delta l/m$ | $\Delta l/m^2$ |
|---------|------|------------|--------------|----------------|
| 0 wt. % | 5.85 | 0 | — | — |
| 0.25 | 5.50 | 0.35 | 1.40 | 5.60 |
| 0.50 | 5.55 | 0.30 | 0.60 | 1.20 |
| 1.00 | 5.00 | 0.85 | 0.85 | 0.85 |
| 2.00 | 4.75 | 1.10 | 0.55 | 0.28 |
| 4.00 | 4.40 | 1.45 | 0.36 | 0.09 |

Table 5 Calculated values of Δl , $\Delta l/m$ and $\Delta l/m^2$ for sample A-2.

| m | I | Δl | $\Delta l/m$ | $\Delta l/m^2$ |
|---------|------|------------|--------------|----------------|
| 0 wt. % | 4.90 | 0 | — | — |
| 0.25 | 5.15 | -0.25 | -1.00 | -4.00 |
| 0.50 | 4.65 | 0.25 | 0.50 | 1.00 |
| 1.00 | 4.60 | 0.30 | 0.30 | 0.30 |
| 2.00 | 4.15 | 0.75 | 0.38 | 0.19 |
| 4.00 | 4.00 | 0.90 | 0.23 | 0.06 |

Table 6 Calculated values of Δl , $\Delta l/m$ and $\Delta l/m^2$ for sample B-1.

| m | I | Δl | $\Delta l/m$ | $\Delta l/m^2$ |
|---------|------|------------|--------------|----------------|
| 0 wt. % | 5.30 | 0 | — | — |
| 0.25 | 5.00 | 0.30 | 1.20 | 4.80 |
| 0.50 | 5.15 | 0.15 | 0.30 | 0.60 |
| 1.00 | 4.75 | 0.55 | 0.55 | 0.55 |
| 2.00 | 4.85 | 0.45 | 0.23 | 0.11 |
| 4.00 | 4.80 | 0.50 | 0.13 | 0.03 |

Table 7 Calculated values of Δl , $\Delta l/m$ and $\Delta l/m^2$ for sample B-2.

| m | I | Δl | $\Delta l/m$ | $\Delta l/m^2$ |
|---------|------|------------|--------------|----------------|
| 0 wt. % | 6.95 | 0 | — | — |
| 0.25 | 7.15 | -0.20 | -0.80 | -3.20 |
| 0.50 | 6.65 | 0.30 | 0.60 | 1.20 |
| 1.00 | 6.00 | 0.95 | 0.95 | 0.95 |
| 2.00 | 5.40 | 1.55 | 0.78 | 0.39 |
| 4.00 | 4.85 | 2.10 | 0.53 | 0.13 |

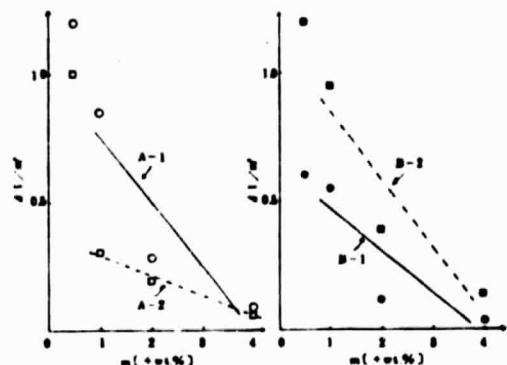


Fig. 4 Plots of $\Delta l/m^2$ versus m according to the case (a).

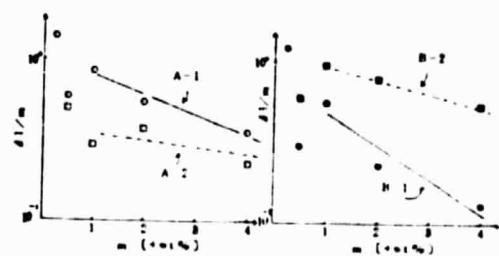


Fig. 5 Semilogarithmic plots of $\Delta l/m$ versus m according to the case (b).

Table 8 Estimated values of k and A appeared in the case (b) and A/k .

| Item | A-1 | A-2 | B-1 | B-2 |
|-------|------|------|------|------|
| k | 0.13 | 0.04 | 0.21 | 0.08 |
| A | 1.05 | 0.38 | 0.78 | 1.10 |
| A/k | 8.1 | 9.5 | 3.7 | 13.8 |

3.2. Analysis of Measured Values

Tables 4-7 give the results obtained when the measured values are organized on the basis of the aforesaid thinking.

Figs. 4 and 5 show the results when they are plotted with respect to cases (a) and (b).

The measured values have a better linearity in case (b), in which /6 the dependence of q and \bar{q} on m is considered, that is, in Fig. 5. Deviations from linearity are evident in the region where small amounts are added and where m is less than 1% by weight. However, this would seem to be attributable to the fact that proportional increases of the potential are impeded because of the influence of the adsorbed ions.

In Fig. 5, the intersections between the gradients of the straight lines and the ordinate express k and A in 3.1 (b). As is clear from equation (5), $\phi - \phi_0$ takes its maximum value, $Ak^{-1}e^{-1}$, when $m = k^{-1}$. Consequently, when k has a larger value, the surface potential will reach its maximum with a smaller amount of deflocculant, but its value will on the contrary become lower. The values of k and A found from Fig. 5 are given in Table 8.

Clays A-1 and B-1, which have fewer adsorbed ions, tend to have a larger k than A-2 and B-2, which have more of them. On the other hand, A-1 and B-1 have smaller A/k values.

3.3. Comparison of Clay and Calcined Alumina

Several types of fine powders are generally used together in monolithic refractories. In connection with this point, we reported previously that alumina exerts a more powerful influence on the flowability of alumina-silica systems [3]. Therefore, the tests conducted at this time were applied also to alumina and the results were compared with the aforesaid results for clay.

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The alumina used in measurements was the same calcined alumina used in the previous report [3]. The measurement conditions were the same as those used for the clay, and the measurement results are shown in Fig. 6. Since there is no influence of adsorbed ions, as in the case of the clay, the changes occur smoothly. In Table 9, these results are organized in the same way as above in 3.2.

In Figs. 7 and 8 these results are plotted according to (a) and (b) in 3.1.

As was true in the case of the clay, (b) gives a better linearity. Moreover, there is a better linearity when the measuring points are divided into two regions: one in which m is small, and one in which m is large. It is believed that this is because secondary and higher terms in m were ignored in the case of (b). Table 10 shows the results obtained when k and A were found from the line in Fig. 8 and A/k was calculated.

The values of k are approximately the same as or larger than those of clay. In particular, k is quite large in (I), the region where small amounts were added. The A values also are about one digit larger than those of clay. It is anticipated from these results that if a deflocculant (in this case SPP) is added to a system in which both clay and alumina are present, most of it will be adsorbed onto the alumina.

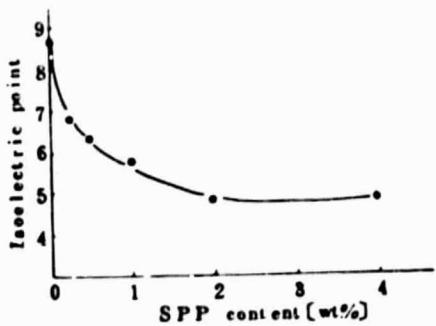


Fig. 6 Isoelectric point of calcined alumina as a function of SPP content.

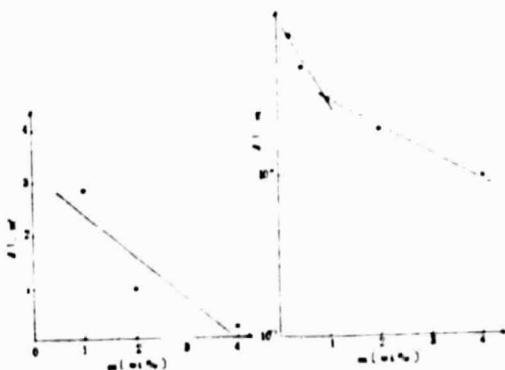


Fig. 7 Plots of $\Delta I/m^2$ versus m for calcined alumina according to the case (a).

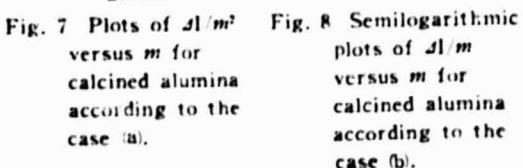


Fig. 8 Semilogarithmic plots of $\Delta I/m$ versus m for calcined alumina according to the case (b).

Table 9 Calculated values of ΔI , $\Delta I/m$ and $\Delta I/m^2$ for calcined alumina.

| m | I | ΔI | $\Delta I/m$ | $\Delta I/m^2$ |
|---------|------|------------|--------------|----------------|
| 0 wt. % | 8.65 | 0 | — | — |
| 0.25 | 6.80 | 1.85 | 7.40 | 29.60 |
| 0.50 | 6.30 | 2.35 | 4.70 | 9.40 |
| 1.00 | 5.75 | 2.90 | 2.90 | 2.90 |
| 2.00 | 4.80 | 3.85 | 1.93 | 0.97 |
| 4.00 | 4.80 | 3.85 | 0.96 | 0.24 |

Table 10 Estimated values of k and A for calcined alumina appeared in the case (b) and A/k . (I) and (II) denote regions where m is less than or more than unity.

| Item | k | A | A/k |
|------|------|------|-------|
| (I) | 0.60 | 9.00 | 15.0 |
| (II) | 0.17 | 4.40 | 25.9 |

4. Summary

We studied the action of deflocculants on fine powders by measuring the changes in the isoelectric point. The following findings were obtained from the measurement results concerning clay:

(1) When extremely small amounts of deflocculant are added (i.e., less than about 0.5% by weight with respect to the clay), the changes in the isoelectric point are strongly influenced by the amounts of the adsorbed ions.

(2) Since the isoelectric point decreases as a result of the addition of SPP, the surface potential increases in the negative direction.

The measurement results were analyzed by using a simple model concerning the adsorption of the deflocculant in this case, and findings were obtained concerning its mechanism of action. The results obtained concerning calcined alumina-clay systems also showed that SPP is adsorbed preferentially onto the calcined alumina rather than the clay.

(This report was delivered at the Eighth Session of the Specialists' Committee on Monolithic Refractories.)

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